Dissertation

Regional Phosphorus Management in Berlin-Brandenburg

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Table of Contents

List of Figures

List of Tables

List of Abbreviations

Al	Aluminum
As	Arsenic
ATP	Adenosine Triphosphate
$C_6H_6O_{24}P_6$	Phytate
Ca	Calcium
$Ca_5(PO_4)_3F$	Fluorapatite
CAL/DL	Calcium Lactate extraction (for plant available phosphorus)
$CaSO_4$	Calcium Sulphate
Cd	Cadmium
CO_2	Carbon Dioxide
Cu	Copper
DGT	Diffusive Gradients in Thin films
DL	Double Lactate extraction (for plant available phosphorus)
DNA	Deoxyribonucleic Acid
ELaN	Entwicklung eines integrierten Landmanagements durch nachhaltige Wasser- und Stoffnutzung in Nordostdeutschland
Fe	Iron
GDR	German Democratic Republic
HF	Hydrogen Fluoride
K	Potassium
kg	Kilogram
l	Liter
LELF	Landesamt für ländliche Entwicklung, Landwirtschaft und Flurneuordnung
mg	Milligram
Mg	Magnesium
mm	Millimeter
N	Nitrogen
Na	Natrium
NADP	Nicotinamide Adenine Dinucleotide Phosphate
O	Oxygen
P	Phosphorus (*Phosphor*)
P_2O_5	Phosphorus pentoxide
P_4	Tetraphosphorus
Pb	Lead
PR	Phosphate Rock
PVP	Pflanzenverfügbarer Phosphor
Rn	Radon
RNA	Ribonucleic Acid
SFA/MFA	Substance/Material Flow Analysis (*Substanz-/Materialflussanalyse*)
SiF_4	Silicon Tetrafluoride
SOM	Soil Organic Matter
STP	Soil Test Phosphorus
t	Metric tonne
Tg	Teragram
U	Uranium
yr	Year
Zn	Zinc
µmol	Micromol

1. Introduction

Since the beginning of life on earth, phosphorus (P) has become an essential component of life's fundamental structures. Its oxidized form (phosphate, PO_4) is a constituent of cell membranes (phospholipids) where it comparts cells and their organelles; it also participates in storing the genetic information (DNA, RNA), mediates the transfer and storage of energy through phosphorylation (ATP, NADP) and plays a role in cell signaling (GTP). In humans and other vertebrates it is an important constituent of bones and teeth. Due to its function in energy transfer, it plays a crucial part in cellular respiration and photosynthesis. In plants an adequate P supply is necessary for seed and root formation, straw strength in cereals, crop quality (Havlin et al., 1998, Whitehead, 2000) and in ruminant animals it is essential for the development of microbial biomass (Whitehead, 2000). Last but not least, it represents a critical nutrient for biological nitrogen (N) fixation (Vance 2001).

The result of its role in biological processes is that P may have strongly promoted and accelerated the diversification of life by enabling the development of higher more energy demanding life forms requiring oxygen (O) for respiration when life was still on a protozoic level. It was proposed that an increased P availability during the Proterozoic era (up to 2250 million years before presence) led to the first photosynthetically active cyanobacterial blooms which eventually was a key factor in causing the oxygenation of Earth's atmosphere (Papineau et al., 2013). This increasing O concentration in turn likely favored the removal of P from solution in oceans by the sedimentation of excess PO_4 as found in authigenic[1] apatite in the shallow ocean seafloor (Papineau et al., 2013).

According to many sources, P in its elemental form (white P) was first discovered in 1669 by Henning Brandt, a German glassmaker, pharmacist and alchemist. It is said that he discovered P when searching for the philosopher's stone using a strong distillation of urine and instead found a luminant matter that has since been called P. This term derives from the Greek word *Φωσφόρος*, which means "light-bearer", which corresponds to the Latin word *lucifer* (Farber, 1966). Elemental P exists in various allotropes with a great diversity of physical properties and chemical reactivity, of which white P also known as tetraphosphorus (P_4) with its tetrahedral structure, is the most common form (Pfitzner et al., 2004). As shown by Henning Brandt, white P can be produced from PO_4 by employing high temperatures and a reducing environment (Schipper et al., 2001). It freely reacts with the O in the air and therefore needs

[1] A mineral or sedimentary rock that was generated at the place where it was observed.

to be stored under anoxic conditions. Even though other forms of elementary P are more stable, they rarely exist due to their high tendency to react with O thereby forming PO_4, which is ubiquitously found (Desmidt et al., 2015).

As with other elements which are important for life, such as carbon (C), N and O, P flows through various biogeochemical pathways. In short, for P the cycle can be best described by starting with its release from the earth's crust as mediated through weathering processes. Subsequently, it is gradually withdrawn from the land into the rivers, or is transported directly by the wind, to finally merge into the sea, where it sediments (Föllmi, 1996). As a result of geological pressure, it is converted to new sedimentary phosphate rock (PR), such as those found in Morocco (Edixhoven et al., 2014). In a process taking hundreds of millions of years, these sediments are uplifted to form new dry land, being exposed to weathering forces once again (Schlesinger, 1997). A smaller share reaches the earth's surface in igneous rock (Smit et al., 2009). In contrast to other elements being of similar importance to life like C, N and sulfur, the P-cycle has no significant gaseous compound, thus reducing its atmospheric transport to particles translocated by winds (Tipping et al., 2014).

In the course of time, human activities have profoundly changed the biogeochemical cycle of P. Especially within the last centuries and decades a new quality of influence has been reached (Filippelli, 2008). Along with this development, natural fluxes were accelerated and new anthropogenic fluxes were introduced. The intensified natural fluxes comprise erosion by wind and water and the subsequent transport by rivers or winds to oceans. This intensification is the result of deforestation and land conversion frequently followed by further soil disturbing activities, such as tillage operations for the cultivation of crops that are grown to supply a rising world population with food and other services. Linked to these transformed areas, new relevant flows of P connected to agriculture emerge such as the application of mineral fertilizer originating from PR, manure application and crop uptake. Entering the supply chain, the agricultural goods produced are eventually converted to waste or excreted after which they are often passed on to either landfills or water bodies depending on the infrastructure involved. The latter process together with the flows stemming from erosive processes can have serious consequences for aquatic ecosystems, for which P, next to N represents a major factor in eutrophication causing dead zones in oceans, which have been doubling in occurrence since the mid-1900s (Altieri and Gedan, 2015). These dead zones are hypoxic areas, the result of massive decay of phytoplankton that thrives on elevated nutrient concentrations. Generally, the P in waste and wastewater flows is often not recycled due to sanitary issues and contamination problems with heavy metals or other toxic compounds.

Thus, today valuable P sources contained in sewage sludge and organic wastes are landfilled, hampering a further use of this resource and causing a further mining of P from PR. As a result of the continuous loss of P from various pathways, mankind has become strongly dependent on PR reserves, not only in order to maintain the production of food, but also that of other agricultural products (Smil, 2000). In addition, the production of phosphogypsum as a side product of PR mining is seen as environmentally problematic (Hentati et al., 2015).
In general, the global demand for P is increasing, although its consumption in developed regions is declining. The reason for this development is a growing population in developing countries and a trend towards a more meat- and dairy-based diet that requires more P for its production (Heffer and Prud'homme, 2009).
About 95% of the global PO_4 production is used in agriculture where most of it is needed for the manufacture of fertilizers (up to 90%). Other applications in agriculture are animal feed additives, pesticides (Cisse and Mrabet, 2004) or glyphosate, being one of the most widespread herbicides (Sviridov et al., 2015). The remainder is used in industry to produce high-grade detergents, cleaning agents, dental creams, toothpaste, baking powder, flame retardants, stabilizers of plastics, corrosion inhibitors, glues, and dispersion agents in paints and numerous other applications (Cisse and Mrabet, 2004; Desmidt et al., 2015; Matsubae-Yokoyama et al., 2009).
As summarized by Filippelli (2011), the intensified P flux, caused by water and wind erosion was estimated to be threefold (Bennett et al., 2001) minimizing the 50% variation following extreme changes in landscapes and erosion during glacial cycles (Tsandev et al., 2008).
The situation described clearly shows the critical importance of P as a resource for today's globalized society in which the natural cycles and fluxes of nutrients have been largely interrupted or accelerated. According to the International Fertilizer Development Center (IFDC), PR reserves, underlying the current rate of production, may be depleted within the next 300-400 years (Van Kauwenbergh, 2010). Hence, although exact numbers on P reserves are not available, the fact that PR deposits, which nourish and sustain the world's population and production, are not everlastingly available represents one of the greatest challenges for mankind.
While P scarcity is a global problem, it is clear that many measures to achieve a more sustainable handling of this resource need to be taken at a regional level. Thus, it is inevitable to analyze regional potentials, shortcomings, requirements, services and structures to obtain a comprehensive picture of usage to improve P management. To put this ambition into practice, the thesis at hand deals with P management in the region Berlin-Brandenburg. As a

consequence of the accelerated and disrupted P flows, in Berlin-Brandenburg large amounts of P are now retained at wastewater treatment plants and, apart from some exceptions, are not further utilized to serve agricultural production (Kern et al., 2008; Theobald and Schipper, 2014). In addition, significant amounts of organic wastes are still collected along with inorganic wastes, making the recovery of the contained nutrients therein, including P, unfeasible (Theobald and Schipper, 2014). Agricultural soils of the region on the other hand, are frequently reported to have negative balances (MIL, 2012) and fertilizers from PR that could potentially be substituted by P recyclates, are applied to land (Kern et al., 2008; Theobald and Schipper, 2014). In addition, relevant P losses from human activity foster eutrophication of the water bodies of the region (Körner, 2002). Today, the knowledge of potentials for improving P use efficiency is rather limited and drivers for the diminishing P use are not sufficiently understood. Also, causes for an inner regional inhomogeneity in soil P availability leading to significant amounts of over and undersupplied land (e.g. Römer, 2013) need to be given further attention. While oversupply is connected to eutrophication, insufficient P in soil leads to inefficiencies in the use of other resources, potentially causing their loss to the environment, as in the case of N. Shedding light on these aspects is needed to conserve this precious resource and safeguard agricultural production and the environment for future generations. Hence, within the framework of the ELaN[2] project, the research assignment was given in order to look for new ways of P management within the region.

This thesis was prepared in the course of the ELaN sub-project 4 "Nährstoffrecycling". It comprises two self-containing articles of which one was published in the Journal *Resources, Conservation and Recycling*. The other one was published in the *Journal of Soil Use and Management*. In the last chapter of this thesis, both articles are jointly presented and reflected in a synthesis and complemented by recommendations for possible future research in the field of P management. In general, no changes have been made in the content of published material. However, on some occasions complementing information was added as a footnote to provide a deeper understanding.

[2] **E**ntwicklung eines integrierten **La**ndmanagements durch nachhaltige Wasser- und Stoffnutzung in **N**ordostdeutschland

2. Research Questions

Based on the problems stated above, two research questions were set to grasp the critical unknowns for an improved management of the resource P in Berlin-Brandenburg. **The first research question is: What are the shortcomings and potentials for improvement of P management in the region Berlin-Brandenburg, which arise from the interplay between different subsystems (e.g. agricultural sector and consumption sector) or factors taking influence from outside the system boundaries?** To analyze these inefficiencies and potentials, it is necessary to identify and quantify the P flows in the Berlin-Brandenburg region and to evaluate the results regarding the improvement of system sustainability. This evaluation was done by detecting internal imbalances (e.g. accumulation and deficits of P in certain sectors) and by identifying pathways through which losses occur. Furthermore, recovery potentials were assessed, and their constraints as well as their corresponding solutions were highlighted.

For the second research question, the agricultural sector was granted a closer look: Can the wide range of P availability in soil, as reflected by soil test P (STP) in the region Berlin-Brandenburg, be related to specific characteristics of the farms or farming systems? To address this question, farm structural characteristics, such as organic or conventional farming, animal husbandry and its intensity, the presence of biogas plants, ownership type and land tenure in Brandenburg were assessed, as exemplified by the situation in the two counties Barnim and Uckermark.

3. State of the Art

3.1 The Phosphorus Cycle and Pedogenesis

The weathering process

Weathering is the natural process by which P is released to commence its biogeochemical cycle. Starting from the very beginning of this cycle, organisms interfere by accelerating or slacking its transition from one step to the other within the cycle. Weathering, for example, is known to be accelerated by the cracking of the original rock by swelling roots as in the case of plants, the exudation of organic acids or their precursors (sugars), or the respiration-related release of CO_2 increasing acidity, as in the case of plant and microorganisms (Newman, 1995; Schlesinger, 1997). At the same time, these organisms may inherently conserve a bioavailable reservoir of P. For example, plants reduce P losses associated with soil erosion by covering soil with their aboveground biomass (e.g. canopy and leaf litter) and stabilizing soil with their belowground biomass (roots). This interaction not only couples the P cycle with that of other biogenic elements like C, N or O but also creates a new fraction of organically bound PO_4 (Walker and Adams, 1958), which maintains P in the bio-available pool (Roberts et al., 2015).

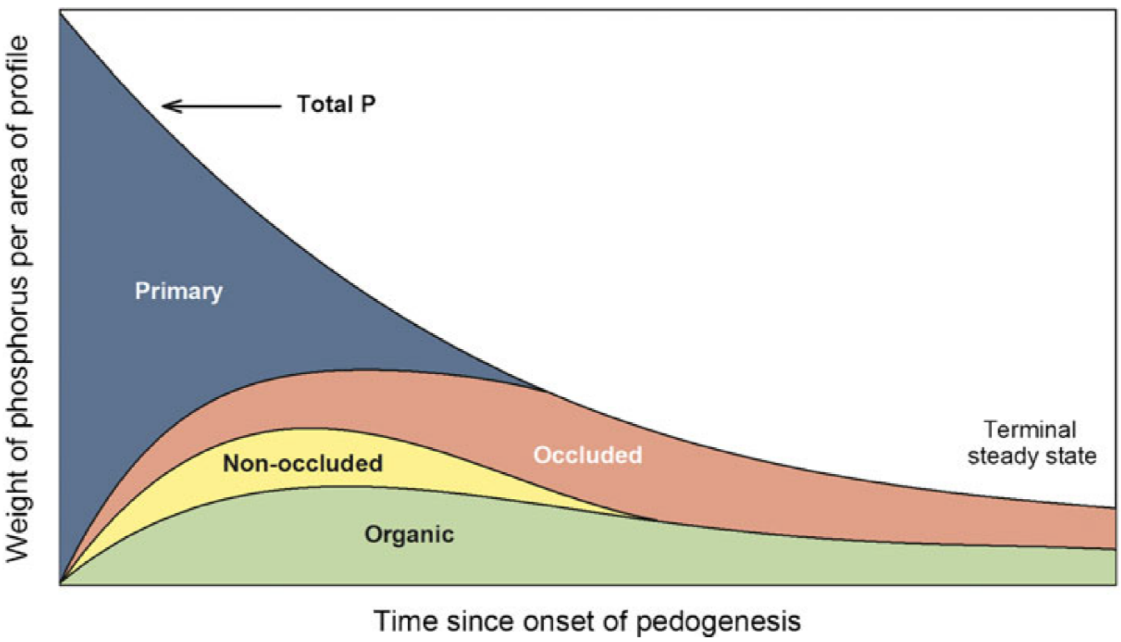

Figure 3.1: Conceptual model by Walker and Syers (1976) of the change in P pools during pedogenesis. The graph was adopted from Turner and Condron (2013).

As presented in Figure 3.1, this process is characteristic during soil formation. Generally, at the beginning of pedogenesis all P is contained in primary minerals like calcium phosphates, of which apatite (mostly fluorapatite [$Ca_5(PO_4)_3F$]) is deemed to comprise 95% of the P (Khasawneh et al., 1980). However, a variety of other Ca minerals are also known to exist (Kruse et al., 2015). As a result of weathering, P is lost from the soil or converted to non-occluded forms, which are either transformed to an organic form or become occluded by physical encapsulation or surrounded by secondary minerals (e.g. iron (Fe) or aluminum (Al) oxides) (Yang et al., 2013). In the final state of soil development, P in soil is dominated by occluded and organic forms. This aging process is reflected in a progressing change of soil type from Entisols to highly weathered Ultisols and Oxisols, with the latter being common in tropical areas. The progressing development described may finally lead to a reduction of plant biomass production and productivity (Wardle et al., 2004). The whole cycle of P including its way after it is withdrawn from soils is depicted in Figure 3.2.

Phosphorus in rivers and oceans, or how the cycle is completed

According to Filippelli (2008), P transport in rivers usually appears either in the particulate or in the dissolved form. The largest share of the particulate P is encased in minerals and is therefore excluded from being taken up by organisms. Due to the alkaline pH and the strong ionic buffering in seawater it remains unaltered even after reaching the oceans. As a consequence, it usually sediments on continental margins and in the deep sea where it rests awaiting subduction or accretion. About 50% of the P entering oceans follows this fate. Some of the remaining P is removed via organic matter that sinks to the seafloor or by marine oxyhydroxides (Feely et al., 1990; Geoffrey Wheat et al., 1996). Some of it is adsorbed on to soil surfaces (oxides) and incorporated into particulate organic matter. P, when adsorbed to soil particles, may be easily removed due to the high ionic strength of the ocean water. Some organic P may be released again by microorganisms. Also, some sedimentary environments along continental margins are suboxic or even anoxic. Such environments favor oxyhydroxide dissolution and the release of sorbed P (Filippelli, 2011).

Generally, the route, starting from a dissolved PO_4 molecule in the ocean to a P-rich phosphorite, is long and rarely travelled (Filippelli, 2011). Reactive P usually reaches the seafloor in organic matter from which it may be released by respiration. As conditions there are usually anaerobic, the mineralization process is driven by sulfate (SO_4) reduction, which generates sulfides (e.g. HS-, H2S) that may result in a further P release by inactivating the major player in P-sorption, namely Fe-oxides. Also the direct release by microbial Fe-oxide reduction may play a role (Roden and Edmonds, 1997). Provided that P is not transported away in water, it may reach concentrations in the pore water that are sufficient to induce the precipitation of fluorapatite. Starting from there it may either reach the earth's surface in the form of igneous mineral after subduction or may be uplifted and again exposed to weathering processes (Filippelli, 2008).

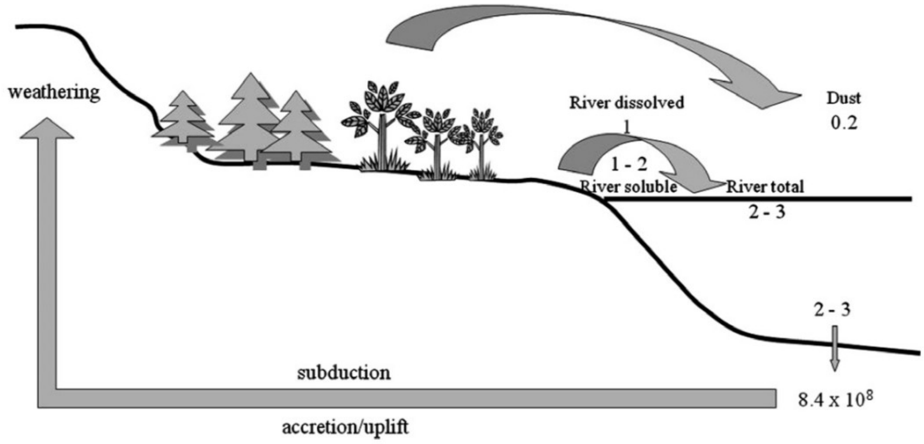

Figure 3.2: Natural cycle of P, depicting inputs to the oceans through water and airborne transport and outputs via sedimentation and recycling via tectonics. Flows are in Tg P/year, the sedimentary reservoir in Tg P. Graph was adopted from Filippelli (2011).

3.2 The Environmental Impact of Phosphorus Use

Phosphorus and eutrophication

As with N, the role of P in terrestrial freshwater and marine environments is a double edged sword. On the one hand, N and P are crucial for ecosystem development, on the other hand, in excess they represent a major thread to aquatic ecosystems in particular causing eutrophication with strong and sometimes severe consequences for the inhabitants of an ecosystem (Elser et al., 2007). For P, eutrophication of surface waters may already appear at concentrations greater than 0.65 μmol of total P/l (= 0.02 mg P/l) (Sharpley and Rekolainen, 1997). Eutrophication of aquatic systems may lead to an increased growth of algae, including a shift in their species composition (Smith, 1998). A high abundance of algae is linked to a reduction of light transition and hence to the loss of submerged macrophytes which are an important habitat for aquatic animals (Körner, 2002). In addition, the decomposing plant material as well as these so called algae blooms lead to a depletion of O that causes fish kills (Carpenter et al., 1998). The explosive growth of toxic algae is reported to be the most pernicious effect of eutrophication causing shellfish poisoning in humans and mortality in fishes and marine mammals associated with marine ecosystems (Anderson, 1994; Burkholder et al., 1992). In freshwater, algae blooms are mainly caused by cyanobacteria which can result in summer fish kills due to anoxic conditions as well as foul odors, unpalatability of drinking water and death in livestock by intoxication, implying also a potential health hazard for humans (Carpenter et al., 1998). Hence, the European Water Framework Directive (Directive 2000/60/EC) commits European Union member states to achieve a good qualitative and quantitative status of all water bodies (including marine waters up to a kilometer from shoreline) by 2015.

Sources of eutrophication

Generally, inputs of P (and N and pollutants in general) to rivers, lakes, and oceans are classified as point or nonpoint sources. In the case of P, point sources comprise wastewater effluents as well as runoff and leachate from waste disposal sites and animal feedlots and also storm sewer outfalls. Nonpoint sources of P, on the other hand, include runoff from agriculture, pastures and ranges, urban runoff and atmospheric depositions over water surfaces (Novotny and Olem, 1994). Point sources of pollutants tend to be continuous, with little variability over time and hence, can be easily monitored and often be controlled by treating the source. Nonpoint sources, in contrast, may also be continuous but are often linked to seasonal agricultural activity or irregular events such as heavy precipitations. They often originate from extensive areas of land and are transported over land, underground, or through the atmosphere to receiving waters. As a result, nonpoint sources of pollutions are difficult to measure and regulate. Their control is even more challenging, since it may affect the daily activities of large numbers of people (Carpenter et al., 1998).

Generally, there are two pathways P enters aquatic systems from agricultural land via nonpoint pollution. (i) One way is the erosion by wind and water which eventually leads to a transport of soil particles to water systems. (ii) The other pathway is via P emission originating from P leaching losses draining from groundwater into surface waters. Together these diffuse inputs where found to account for about 30% of all P emissions in Germany (Umweltbundesamt, 2006). Of these two pathways the first one usually is most important, although, especially in drainage systems, the latter can be very significant (King et al., 2015). Overall, losses can occur in either particulate (>0.45 mm) or soluble form (<0.45 mm) of P. While the accumulation of P in both inorganic and organic forms can, through the application of mineral or organic fertilizers, lead to an increased transfer of P into waters through leaching and runoff, the organic fertilizers are frequently reported to cause greater P emissions to the environment (Borda et al., 2011; King et al., 2015). Aside from P from manures being a flow of P recycling back to the fields, the above observation is even more unfortunate, since in many countries of Europe the agro-environmental guidelines for manure and slurry applications are strongly based on N crop needs which therefore favor P supply to exceed crop demand (Goodlass et al., 2003) as its N:P ratio is generally lower than that of plants (Borda et al., 2011). The measures to reduce diffusive P emission from agricultural land are various. To prevent losses by runoff and erosion, measures like the maintenance of a soil cover, contour plowing, and windbreaks have been suggested (Dotterweich, 2013). Subsurface transport, on the other hand, was found to be promoted by e.g. preferential flow (which is usually stronger in fine textured soils), a low P sorption capacity (which is usually weaker in coarse textured soils) and reducing conditions (which are for example caused by a shallow ground water table) (King et al., 2015; Verloop et al., 2010). For both pathways, high P levels, the timing, placing, rate and type of P application, hydrologic and climatic variables are relevant (King et al., 2015; Reijnders, 2014).

Trace elements in fertilizers and sewage sludge

There is concern that trace elements such as arsenic (As), cadmium (Cd), lead (Pb) and uranium (U) stemming from impurities in P fertilizers may cause environmental and health risks (Jiao et al., 2012; Schnug and Haneklaus, 2015). Problems with impurities in PR and thus its products, such as fertilizers and phosphogypsum, occur in PRs that originate from sedimentary processes (Roessler, 1990; Scholte and Timmermans, 1996), while usually pollutant-free PR sources from igneous deposits are scarce and often contain less than 5% of P_2O_5 (Smit et al., 2009). Many of these trace elements like Cd, Pb, zinc (Zn) and U, are known or hypothesized to substitute for Ca in crystallographic spacings (Altschuler, 1980; Rutherford et al., 1994).

However, not only mineral P fertilizers have raised concerns. Throughout the last decades the application of sewage sludge has also been subject to research and political debates (Baize, 2009; Kabbe et al., 2014). In sewage sludge, trace metals such as Cd, chromium, copper (Cu), mercury, nickel (Ni) and Zn are often undesirable substances next to organic pollutants and pathogens (Schoumans et al., 2015; Wahid et al., 2008; Wani et al., 2007). While organic pollutants are, by their nature, highly diverse and therefore not easy to assess in their impact on health and environment, they can easily be eliminated by the combustion of sewage sludge. Trace elements, however, may remain problematic and require an additional process of extraction (Desmidt et al., 2015; Mehta et al., 2015; Schoumans et al., 2015). As with P fertilizers, concentrations of trace elements in sewage sludge vary significantly depending on their origin. Hence, critical levels for contaminants have been established which are currently under re-evaluation in Germany.

Cadmium

In P fertilizers, Cd impurities are of greatest concern, since it is one of the most toxic trace elements with high phyto-availability (Baize, 2009; Jiao et al., 2012). In Europe about 55% of the Cd in soil was reported to be derived from P fertilizers, while another 40% originated from atmospheric deposition (Pan et al., 2009). These figures are similar to estimates for the US while in China atmospheric deposition was by far the largest source (Chang and Page, 2000; Luo et al., 2009). Further, it was shown that the amount of Cd in topsoil in European countries is closely correlated with the distribution of P which suggests that its input into agricultural soils is connected to P fertilizer use in intensive agriculture (Pan et al., 2009). The mobility of Cd in soils is influenced by the soil pH, organic matter content and components of solid phase minerals (Tiller, 1989). Acidic soil conditions, for example, foster the availability of Cd, while a high soil organic matter (SOM) content reduces its toxic effects (Grant et al., 1999). Also other elements (e.g. Cu, Ni, selenium, manganese and P) can interfere with the uptake of Cd (Pan et al., 2009). Research shows that the Cd availability to plants is related to the availability of P, meaning that the total soil Cd content is a bad indicator for its uptake in plants (Chien et al., 2010). As concluded by Chien et al. (2010), more research, including field experiments, is needed to elucidate e.g. conflicting reports from literature on liming and Cd uptake. However, literature suggests that Cd application along with P fertilizers may not result in an increase in soil Cd if concentration in the fertilizer is below 10 mg/kg. Higher concentrations in combination with intense application of P fertilizers, on the other hand, may result in a slow accumulation of Cd in soil. The accumulation of other fertilizer-borne toxic elements, like As and Pb, in contrast, seems to be limited even under long-term P application (Jiao et al., 2012). Similar assumptions may be drawn regarding Cd contained in sewage sludge.

Uranium

The concentrations of Uranium (U) in the PR rank at such high levels that the U recovery from phosphoric acid production, mainly for fertilizers, started in the early 1950s and lasted until the early 1990s when direct mining of U became more profitable (Guida, 2008). The toxicity of U is synergistically enhanced by Cd. Furthermore, its decay products are also of considerable radiological and chemical toxicity (Thomas, 2008). According to different authors, the extractable U content of German agricultural soils is four times higher than that of forest soils (Huhle et al., 2008; Setzer et al., 2011). Enrichment in soils can be regarded as problematic when crop land is converted to building areas. As radon (Rn), deriving from the radioactive decay of U, can diffuse through cracks in the foundation of buildings, where, in contrast to its emission in fields, it can accumulate and pose a threat to human health (Moinester and Kronfeld, 2014). Generally, the uptake of U by plants and its transfer into the food chain is not regarded as critical (Gramss et al., 2011; Kratz et al., 2008). However, there is evidence from several studies that U from fertilizer application reaches water bodies in Germany and other countries (Schnug and Haneklaus, 2015) and its occurrence in shallow groundwater was shown to correlate with that of nitrate (Smidt et al., 2011). This can be explained by the fact U is often applied together with N in fertilizer. Also, in the form of uranyl-carbonate, U reaches a high mobility in soil resembling the behavior of nitrate in its movement through the soil matrix. In addition, in the presence of nitrate, U (IV) is oxidized to U (VI) and subsequently transported by soil water (Wu et al., 2010). The share of U in groundwater stemming from fertilizer application depends on the respective background concentration in soils and may reach up to more than 90% in naturally low U environments. However, from a technological standpoint U can be easily removed from drinking water (Riegel and Höll, 2009). Summarizing, it can be stated that the application of P fertilizers releases significant amounts of U into the environment, but the exact consequences for health and environment are not yet clear.

Environmental problems of phophogypsum

Along with the beneficiation of PR, large amounts of phosphogypsum are produced as a byproduct, i.e. about 4-6 t of phosphogypsum for each ton of phosphoric acid (IAEA, 2013). With a pH of 1, initially highly acidic due to the contained sulfuric acid it mostly consists of, calcium sulphate dihydrated ($CaSO_4 \cdot 2H_2O$) or hemi-hydrated ($CaSO_4 \cdot ½H_2O$). Other problematic substances contained are fluorides, sulphates, natural radionuclides, metals and other trace elements. While its acidity is largely reduced by dewatering and weathering in storage piles, phosphogypsum may emit significant amounts of radioactive Rn gas stemming from radioactive decay and fluorine compounds, such as SiF_4 and HF. In addition, if exposed to wind, the spread of fine phosphogypsum particles can be problematic. Also, soils and ground water are affected by acidic and metal-rich infiltrations (Hentati et al., 2015). As for P fertilizers, the emission of Rn is connected to the decay series of U which as a stable and

unstable isotope is also found in PR and its byproducts such as phosphogypsum, as well as a variety of other radionuclides (Baxter, 1996; Olszewski et al., 2015).
In order to deal with the high amounts of phosphogypsum, it is discharged to water bodies, backfilled in mine pits, and dry or wet slacked, all of it resulting in severe consequences for the environment (IAEA, 2013). Hentati et al (2015) outlines that alternative valorizing possibilities have been proposed as a solution to reduce storage costs and the negative impact on health and environment, and are already in practice. One of them is the incorporation of phosphogypsum in construction material instead of natural gypsum. The resulting products (e.g. cement) are said to exhibit good mechanical properties and very low levels of radionucleotides. Another approach that has also already been widely practiced for decades, is the use as a soil amendment in agriculture of a supply of Ca, P and SO_4, or the increase of soil pH. Furthermore, it has been applied alone or in combination with synthetic organic polymers for combating runoff and erosion in agricultural soils suffering from strong rains. The recommended amounts for the application to agricultural soil range between 500 and 1000 kg/ha. However, while such an approach would make use of P, it may be problematic due to health and environmental issues. Also, as the impurities of PR are likely to grow, hazards connected to its contaminants are noteworthy (Cordell et al., 2009).

3.3 Phosphorus in Plant Nutrition

P, next to at least 14 other mineral elements, is needed by plants to complete their life cycle, while another four mineral elements are considered as being potentially beneficial. Due to its role as a common growth limiting nutrient in natural ecosystems and agroecosystems, it is considered to be a macronutrient (Marschner, 1995). Generally, plants take up P from the soil solution in the form of the orthophosphate ions $H_2PO_4^-$ and HPO_4^{2-}, with the latter being of less importance (Syers et al., 2008). The uptake of these inorganic P-forms from the soil is influenced by several factors comprising soil and plant inherent properties. Controlling factors in this process are e.g. crop and soil management, the extent and size of the root system, the concentration of P in soil, the P buffer capacity, the soil texture, the pH of the soil solution, the presence of other elements such as Al, Fe and Ca, the water supply, the aeration of soils, the temperature, the soil structure, the amount and quality of SOM, plant-species specific adoptions, and the presence and composition of the microbial flora such as bacteria and mycorrhizas. It is important to note that all these factors interact in specific ways with each other (Römer, 2006; Syers et al., 2008).

A well-developed root system, for example, provides a better access to water, P and other nutrients due to a larger root soil interface. However, in addition to the size, its distribution along different parameter gradients is also of significance. Topsoils, for example, may contain more plant available nutrients, whereas subsoils are less prone to shortages in the water supply. One of the most influential variables is the soil texture, which influences a broad range of parameters. It affects the P buffer capacity, the quality and quantity of SOM, the presence and activity of other relevant elements (Al, Fe and Ca), the soil structure, the water and air supply, and so forth. For a detailed and comprehensive discussion and review on this the reader may refer to additional literature (Brady and Weil, 2007; Syers et al., 2008).

In soil, PO_4 is transported to the root surface by mass flow (flow of water containing PO_4) or diffusion. Furthermore, soil PO_4 may be intercepted by growing roots. The take up of nutrients by interception and mass flow together, account for less than 5%. In contrast, the diffusion of nutrients to the root surface is regarded as the main source of nutrient acquisition. This diffusive movement is mediated by a concentration gradient, which is created by the removal of nutrients from soil solution (Barber, 1984). A crop grown on a field may take up 20 to 40 kg of P/ha in the course of a growing season. This amount is much larger than the actual quantity of less than 0.2 kg of P/ha found in soil solution to a depth of 30 cm. This large difference to the supplied P is explained by the ability of the roots to absorb P at very low concentrations, on the one hand, and by desorption of P from the solid phase of the soil on the other (Frossard et al., 2000).

Thus, the amount of P available for plant uptake in soil solution depends on the sorption-desorption characteristics of a soil in combination with the size of different soil P pools. Syers et al. (2008) proposed a model which consists of four different soil pools (Figure 3.3) reflecting a continuum of bonding energies for P that represents the nature of its physical association with the soil components in which P is retained. The first pool represents the P in soil solution. It is immediately plant available. It is followed by the second pool that is readily extractable and held on sites on the surface of soil components, where it is considered to be in equilibrium with P in the soil solution. This pool readily replenishes the P in soil solution that is taken up by plants. Both of these pools are subject to measurements by routine soil tests, which access this P to different extents depending on the reagent used (Roberts and Johnston, 2015). The third pool represents the less readily extractable P that is more strongly bonded to soil or is located within the matrices of soil components as absorbed P. It can become plant-available over time. Generally, P can be reversibly transferred between all of these three pools. The fourth pool is characterized by a low or very low extractability of P. In this pool, P is very strongly bonded to soil compounds, or is part of the soil mineral complex. It may also be unavailable due to its position within the soil matrix. P found in this pool becomes plant available at a very slow rate, often over periods of many years. When a fertilizer with water-soluble P is added to a soil only a very small proportion remains in the soil solution. The majority of P is distributed between the readily available and the less readily available pool by adsorption and absorption, while another small fraction may be initially precipitated in some calcareous soils (Syers et al., 2008).

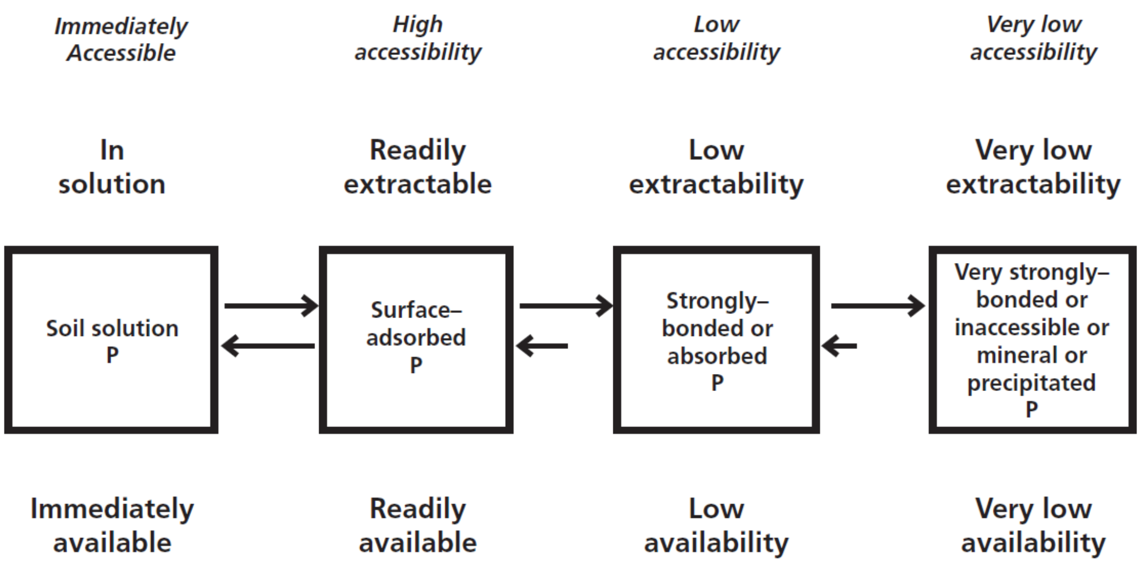

Figure 3.3: Conceptual diagram adopted from Syers (2008) for the inorganic forms of P in soils categorized in terms of accessability, extractability and plant availability.

However, P in SOM can also constitute a relevant pool that represents a source for plant nutrition. Due to the ubiquitous occurrence of P in life, it derives from microbes, fungi, plants and animals, organically bound P can range between 20 to 80% of the total P in the soil surface layer, of which the majority of about 40% may be included in the inositol P fraction which originates from *myo*-inositol hexakisphosphate (phytic acid or phytate; $C_6H_6O_{24}P_6$). Phytate is a storage compound for P in plants, especially in their seeds. Another 7% is found in lipids and nucleic acids (Dalal, 1977). This organic P is known to play a crucial role in the dynamics and cycling of soil P and in order to become plant-available, this fraction first needs to be mineralized by hydrolyzation from the organic matter (Helal and Dressler, 1989; Walker and Syers, 1976). The mineralization process is mediated by microorganisms and plants which can excrete phosphatases (Tarafdar and Claassen, 2003, 1988). Steffens et al. (2010) showed that various crop species are able to take up P from Na-hexaphytat. A very good performance (relative to the $Ca(H_2PO_4)_2$ treatment) was observed for rape seed (*Brassica napus* L.), pigeon pea (*Cajanus cajan* (L.) MILLSP.) and phacelia (*Phacelia tanacetifolia* L.), followed by maize (*Zea mays* L.) and white lupin (*Lupinus albus* L.). Sugar beet (*Beta vulgaris* L.), Mexican sunflower (*Tithonia diversifolia* (HEMSL.) A.GRAY), wheat (*Triticum aestivum* L.), buckwheat (*Fagopyrum esculentum* L.) and rye (*Secale cereale* L.), were less successful, with rye exhibiting the lowest performance.

However, similar to inorganic P, organic PO_4 may be adsorbed to mineral soil surfaces. Also, factors controlling the mineralization of organic matter may affect P availability (Ognalaga et al., 1994). It should be noted too that organic P is not captured by routine soil tests used in agriculture (Steffens et al., 2010).

Soil phosphorus legacy

At the end of the 1800s, at the time of burgeoning P fertilizer use, the level of P in soils of Western Europe was still relatively low (Csathó and Radimszky, 2012). Following this, within the course of the green revolution, during the second half of the 20th century, the consumption of PR reserves drastically inclined. This development was mainly driven by the increasing use of P fertilizers in the Soviet Union, Western Europe and North America (Cordell et al., 2009). However, for Europe, the increased use of P fertilizers in Central and Eastern Europe began decades later than in Western Europe. As a result of this, and lower livestock numbers, P balances in Eastern Europe were far lower in the 1960s than in the 1980s, which consequently resulted in a lower accumulation of P in these regions. The distinct difference between Eastern and Central Europe and Western Europe, has been further promoted by the breakdown of the Soviet Union due to economic difficulties for the farmers of Eastern and Central European countries and the decrease in subsidies received (Csathó and Radimszky, 2009). Thus, also in Germany this similar situation led to different P balances in East and West Germany until the fall of the Soviet Union (Harenz et al., 1992). And also thereafter, P balances in East Germany were lower than those in West Germany, reflecting the contrasting livestock densities, which are regionally high in West Germany (Eurostat, 2015; Grunert, 2013; Römer, 2013; Zimmer and Ellmer, 2012).

Nonetheless, it is clear that in the past, a substantial legacy of soil P has been built up in whole Germany that now represents a large secondary P source, which could be utilized to substitute P applications to land, while at the same time it may as always be regarded as problematic in terms of environmental pollution (Rowe et al., 2015). In particular, the increase of P in ground water by legacy P is seen as problematic since ground waters continually contribute nutrient loads to river base flows (McDowell et al., 2015). Despite this, however, legacy P may be regarded as beneficial as it represents an insurance against possible future price peaks or scarcity of P fertilizers (Rowe et al., 2015).

Table 3.1: Global and regional estimates of legacy P in relation to current and future crop demand and fertilizer use up to 2050 and the potential years of crop P supply according to two scenarios of soil P availability (Rowe et al., 2015).

Region	Legacy soil P 1965–2007 Tg (kg/ha)	Crop demand 2007 Tg (kg/ha)	Crop demand 2050 Tg (kg/ha)	Fertilizer P use 2012 Tg (kg/ha)	Supply (20 %)[1] 2008–2050	Supply (50 %)[1] 2008–2050
Western Europe	105 (1115)	0.93 (9.9)	0.98 (10.4)	0.93 (9.9)	21	54
Eastern Europe	86 (430)	0.78 (3.9)	0.88 (4.4)	0.69 (3.4)	20	49
North America	105 (465)	1.98 (8.8)	2.86 (12.7)	2.06 (9.1)	7	18
Latin America	82 (480)	1.51 (8.9)	2.24 (13.2)	2.66 (15.7)	7	18
Asia	373 (690)	5.41 (10.0)	8.55 (15.8)	12.73 (23.5)	9	22
Africa	40 (160)	0.77 (3.1)	2.05 (8.3)	0.61 (2.5)	4	10
Oceania	26 (560)	0.12 (2.5)	0.30 (6.5)	0.58 (12.6)	17	43
World	815 (550)	11.5 (7.6)	17.9 (11.8)	20.3 (13.3)	9	22

[1]The number of years legacy soil P (1965–2007) would meet the annual crop demand (2008–2050) if 20 or 50 % of that legacy P was plant available. 20 % of legacy soil P amounts to 163 Tg of P and 50 % of legacy soil P amounts to 408 Tg of P

According to Sattari et al. (2012) the global accumulation of legacy P between 1965 and 2007 averaged at ca. 550 kg P/ha, which suggests that 815 Tg of P from P application has accumulated in soils. As stated by Rowe et al. (2015), in comparison with the current amount of global P fertilizer use of about 20 Tg P/year and a projected global crop demand until 2050 (ca. 18 Tg P/year), soil legacy P could in theory substitute the use of P fertilizer for about 9-22 years, depending on the plant availability of past P applications (20 or 50%). For Eastern and Western Europe these numbers are even higher, estimating a possible supply of P of up to 20-49 and 21-54 years (Table 3.1). However, the flaw in such calculations becomes apparent when considering the fact that P has never been homogeneously applied to soils. For instance, in the case of Europe, Tóth et al. (2014), report lower STP values in the East and West Mediterranean regions, whereas in regions with high livestock densities along the North Sea in Denmark, the Netherlands, Belgium and Northern Germany, STP values were found to be highest. Also, in addition to the difference in P loads, distinct differences in soil types also influence the plant availability of past P applications.

On a global scale, it was suggested that 30% of the global cropland area was affected by P deficiency in 2000. This finding is connected to the observation that in many developing countries in Africa, Asia and Latin America, soils have been continually depleted over the years as a result of low P inputs (MacDonald et al., 2011).

As outlined by Rowe et al. (2015) next to a reduction in P fertilizer use, different strategies would be needed to access legacy P captured in soils. Such strategies comprise (i) soil, crop and nutrient management, (ii) plant breeding and (iii) microbial engineering.

The critical plant available soil phosphorus level –finding the right amount

As indicated in the previous chapter, not only from an economical point of view, but also from the perspective of sustaining crop production on the one hand, and preventing diffusive losses on the other, finding the right critical soil level for P is essential. The first work on efficient fertilizer use was conducted by Mitscherlich (1909) who demonstrated a curvilinear relationship between soil test P with respect to the supply of P and oat yields. The results disclosed in this study represent the basis for soil analyses and fertilizer application for the past decades (Römer, 2009). Today, many different soil tests have been calibrated, using the relationship described by Mitscherlich, by identifying the value of plant available P at which at least 90% of the maximum yield can be determined. In Europe alone, at least 10 different soil tests on the basis of different chemical extractants are employed to determine plant available P fraction in soils. This situation largely impedes meaningful comparisons between different regions, the exchange of scientific data across borders and the development of a common European recommendation scheme that could improve the management of P. Hence, further efforts are being made to improve various different recommendation systems with various soil and site specific interactions (Jordan-Meille et al., 2012). However, despite the differences described for the extractants, as a matter of course the main structure of recommendation systems which are based on these STP values remains very similar all over Europe and other parts of the world. Usually they define ranges of insufficient supply, sufficient supply and excessive supply of plant available P, with the majority comprising 5 different ranges defining very low, low, medium or recommended, high, and very high amounts of STP in soil. Some of these recommendation systems also integrate additional information on soil properties such as pH or other parameters (Jordan-Meille et al., 2012; Tóth et al., 2014). For example, in Brazil where soils are generally poor in plant available P, cation exchange capacity, base saturation, base sum, exchangeable Al, Ca/magnesium (Mg), potassium (K) and P levels, sodium (Na), saturation and electrical conductivity are used for the recommendation of P applications for fertilizers (Palhares de Melo et al., 2001).

In Germany different recommendation systems with mostly 5 ranges are employed, which represent variations of the “VDLUFA-Standpunkt zur Phosphordüngern von 1997” (Römer, 2013). Depending on the state, they are supplemented with information on additional soil properties or allow the use of an additional soil P test. In the case of Brandenburg, Mecklenburg-Western Pomerania and Saxony-Anhalt the pH and/or the $CaCO_3$ content is accounted for. Also, recommendations are given for STP values determined by double lactate extraction (CAL) or calcium acetate lactate extraction (DL) method (LVLF et al., 2008). Despite the widespread application of chemical extractants to predict plant-available P, their performance was shown to be relatively inconsistent (e.g. Mason et al., 2010; McBeath et al., 2005). According to Six et al. (2012) this may be caused by the fact that when using these methods the soils are often extracted in a very different state from natural rhizosphere conditions (e.g. ionic strength and composition, pH, soild:liquid ratio). Hence, new methods using different approaches may be valuable in obtaining results that better correlate with plant uptake. A simple method that was shown to better predict P uptake by a number of crops is the 'diffusive gradients in thin films' (DGT) method (Mason et al., 2010; Six et al., 2013, 2012). This method works without extractants, by simply deploying a layer of ferrihydrite binding gel with a strong affinity for P which is placed behind a diffusive hydrogel layer and an overlying protective filter membrane (Panther et al., 2011).

The flaw in today's recommendation systems is that usually, environmental aspects are not considered in such recommendations, leading to an excessive supply of P to agricultural soils (Jordan-Meille et al., 2012; Tóth et al., 2014). Also, data published by Csathó and Radimszky (2009), suggests that these recommendation practices are often not put into practice by farmers. One reason for this is the spatial separation of livestock production and crop production. In addition, Römer (2013) suggests that recommendation systems in Germany overestimate the amount of STP that is required to ensure crop production and that diverse political motivations may hinder the adoption of lower critical values as a basis for fertilizer recommendations. The observation that critical values could be adjusted towards lower values is also supported by findings made by other authors (Hege et al., 2008; Kuchenbuch and Buczko, 2011; Lorenz, 2004). However, the fact that the different soils types and climatic regimes present in Germany may require different critical values must be considered.

The phosphorus scarcity debate

The research of Ulrich and Frossard (2014) on historical literature revealed that fears about food security as a consequence of P scarcity are almost as old as the discovery of the essentiality of P for plant growth, e.g. Justus von Liebig already wrote that England's excessive bone imports would rob "all other countries of the condition of their fertility" (Blakey, 1973). However, as concerns about depletion were always alleviated by new estimates on the available P reserves and resources, no measures were undertaken to improve the efficiency and effectiveness of P use (Ulrich and Frossard, 2014).

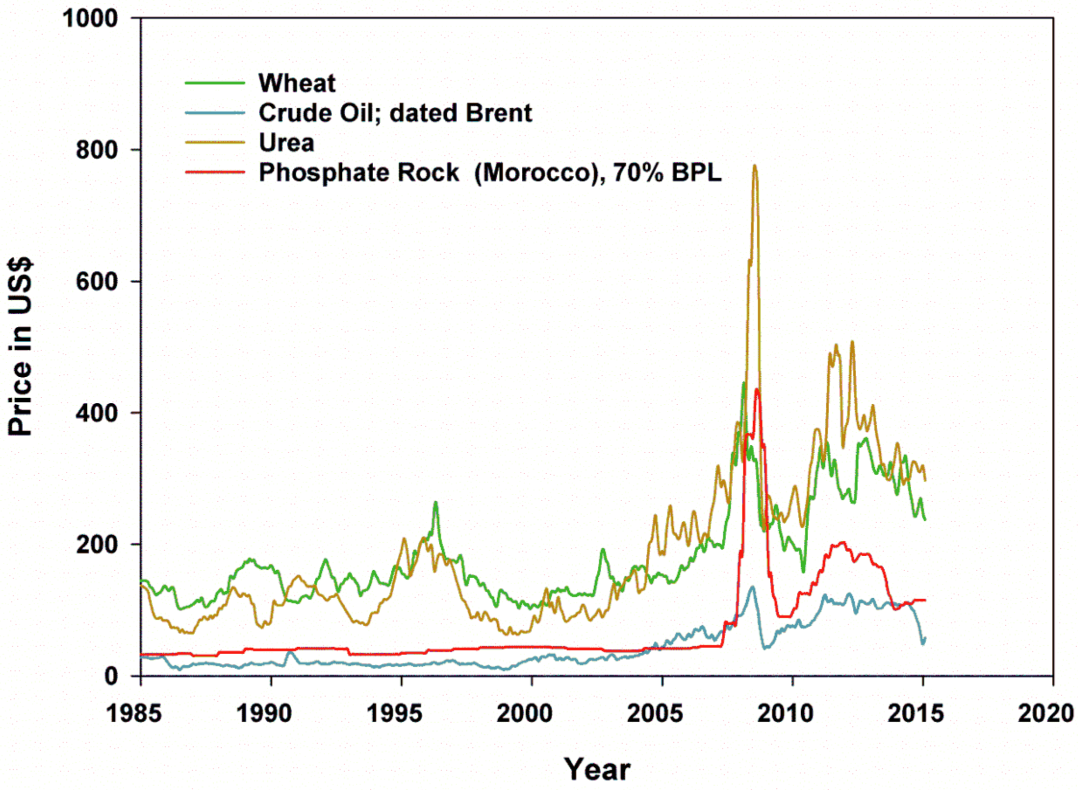

Figure 3.4: Price development of phosphate rock (PR) and other commodities. Data obtained from IndexMundi (2015).

During the last few years, the perspective on the scarcity of P has changed substantially again towards a more apprehensive view of the issue. It started with a research paper by Cordell et al. (2009), which caught the attention of a large audience, as it was proposed that "peak P" in analogy to "peak oil" (Hubbert, 1949) would appear in the near future (2033). The term "peak" as used by Hubbert describes a point in time of maximum extraction after which extraction will decline, due to rising costs in mining caused by more difficult accessibility and a lower grade (quality) of the ores. Factors that determine the accessibility are the depth, the thickness and the geological disturbance of the ore (Edixhoven et al., 2014). However, in response to the discussion on scarcity, new, larger figures were published on the size of PR reserves – the resources[3] that are economically valid to be mined (Jasinski, 2011), which would make the statement by Cordell et al. (2009) obsolete. These corrections stem chiefly

[3] PR of any grade that may be produced at some time in the future. It includes the part that is referred to as reserves (Van Kauwenbergh, 2010).

from higher estimates on the available reserves in Morocco and West Sahara, which was occupied by Morocco in 1975. The amount of reserves there increased from 16 to 65 Gt, which now would make about 75% of the total reserves as registered by the US Geological Survey. However, as assumed by Edixhoven et al. (2014), these new numbers were “in all likelihood” simply a restatement of resources as reserves which was concealed by some transformation calculations. Thus, the credibility of the information remains uncertain. Nevertheless, it may be argued that the term reserves is dynamic as it is based on estimates on technology, potential market developments, prices and costs of production, the accuracy of the exploration process and the planning horizon of companies (Van Kauwenbergh, 2010). Also, one should bear in mind that information on the presence of reserves is given by private companies or states and thus may be subject to manipulation. In any case, according to the USGS the world resources of PR are more than 300 billion tons (Jasinski, 2015) and as presumed by Ulrich and Frossard (2014) new resources and reserves of P-Rock may be found that will postpone the day of depletion.

The presence of additional P ores that have not yet been identified and considered for exploitation is more than likely. In particular, offshore PR have not been granted much attention although their existence has been known for quite some time. According to Ulrich and Frossard (2014) and Jasinski (2015), large resources of PR have been identified on continental shelves and on seamounts in the Atlantic Ocean and the Pacific Ocean and dredge mining of PR deposits offshore from Namibia and New Zealand was planned to commence before 2020. However, it remains questionable if these resources will be exploited in a practical, economically and environmentally acceptable way (Walan et al 2014). While the first two points may be subject to future price developments, it is conceivable that environmental costs may probably be high and also hard to gauge, because of insufficient knowledge of the respective ecosystems.

Figure 3.4 shows the price development of PR and other selected commodities in the last 30 years. As it shows, the price of P is partly coupled with that of other commodities that are connected to its production (crude oil) and that share the same resource for its production (as with oil for urea and wheat) or that are linked to its application (wheat). However, according to Weber et al., (2014) other factors also clearly play a role in price development. It becomes apparent too that after the high price rise in 2008, prices have not returned to the low level until after 2008. A preliminary model presented in Weber et al., (2014) identifies a variety of different factors that influence the price of mineral fertilizers in general (Figure 3.5). These factors may be driven by a growing population in developing countries including their changing diet (more meat, dairy products, vegetables, fruits, and vegetable oils), and an enhanced use of biofuels, which in turn can influence fertilizer use (FAO, 2008; Terazono and Farchy, 2012; Weber et al., 2014). Also, rising prices for agricultural products or other factors leading to a growth of agricultural production eventually resulting in an increased consumption of fertilizers may cause higher P prices (Terazono and Farchy, 2012). Hence, it is clear that an increased efficiency and effective use of P is needed, even though the time left with PR remains subject to speculation, (Reijnders, 2014).

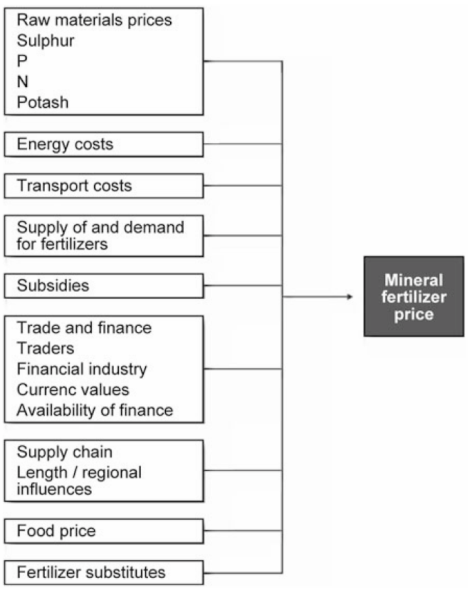

Figure 3.5: Factors influencing the mineral fertilizer prices taken from Weber et al. (2014)

As a result of the finite nature of P resources, Ulrich and Frossard (2014) compiled different motivations for a more deliberated handling of the world's P resources from different authors: 1. geopolitics and supply independence, 2. excess P in the environment, 3. regional food insecurity due to phosphate-deficient soils, and 4. global distributive justice, referring to economic and socio-technical P imbalances.

4. Phosphorus Flows in Berlin-Brandenburg, a Regional Flow Analysis

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Abstract

Phosphorus (P) is a virtually finite nutrient element that cannot be substituted by any other substance. To overcome limited supply of mineral P deposits and to contribute to its sustainable management, a better knowledge on P flows is needed. In this study, a substance flow analysis for P was conducted for the German region of Berlin-Brandenburg. The aim was to create a basis to improve P management in various societal sectors such as forestry, agriculture, human consumption and waste, wastewater management and urban soils. We found that within the system boundary under study, agricultural soils showed the largest negative balance (-3,617 t P), which was connected to low P fertilizer application and low livestock densities. Forest soils followed (-424 t P) possibly as compensating inputs by weathering and atmospheric deposition could not clearly be defined. From recent literature it was concluded that atmospheric deposition to soil pools has been overestimated in many P substance flow analyses and that forest productivity may become more P limited. The greatest P accumulations in soils were found in landfills (3,492 t P) and urban soils (664 t P). The biggest flows came from agriculture, followed by human consumption. The efficiency of agricultural soils was high (127%), as reflected by a negative soil balance due to the low livestock density and input of mineral P. Agricultural soils were the largest contributor of P emissions to water bodies. For the region, evidence showed that weather variations were a major driver for P-removal by the main crops (50% range) influencing the overall P removal by about 46%. Based on climate change projections for the region, we discussed possible future implications for P flows of the region. The recovery efficiency of P from wastewater was very high (91.5%), but the recycling to agriculture was very low (11%), neglecting the large potential of P in wastewater. Also, the recycling of P into organic wastes has been hitherto insufficiently considered, as most organic wastes were not collected separately.

5. Phosphorus Availability and Farm Structural Factors: Examining Scarcity and Oversupply in North-East Germany

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Abstract

Assessing factors influencing phosphorus (P) availability in soils is important in preventing its overexploitation and excessive application in agricultural systems. Despite high historical P applications in the Federal State of Brandenburg (Germany), county data on soil test P (STP) reveal considerable disparities in soil available P. In addition, negative soil balances as a result of small mineral P and manure inputs have been observed, raising questions about the factors leading to this situation. Our work focused on identifying possible causes operating at the farm management level by conducting a letter survey in two administrative districts of Brandenburg, the counties Barnim and Uckermark, linking farm management factors (ownership type, farm size, land tenure, animal husbandry with or without grassland and its intensity, presence of a biogas plant and organic production) to farmers' self-indicated levels of STP. Small- to medium-sized individual farms tended to have (very) high STP, while large partnership farms and companies/cooperatives were sensitive to factors resulting in low STP. Farms with low shares of land ownership, the presence of grassland, extensive cattle farming and stockless organic farming had lower STP. On the other hand, biogas plants, partly in combination with intensive livestock (cattle) farming, were associated with larger STP. It was concluded that more care should be devoted to the design of agricultural policies and that further (inter- and transdisciplinary) research on this topic is needed.

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6. Synthesis

The negligence of a proper management of P flows has generally led to an increasing waste of the earth's limited P resources, which is expressed in the excess accumulation of P in different areas such as landfills, agricultural soils, urban soils, or water bodies, where in the latter case it leads to the eutrophication of water bodies. On the other hand, P deficits may also appear as a result of an inappropriate management. To uncover the extent of this development as found in the region of Berlin-Brandenburg, two research questions were set. The first research question aimed at analyzing the whole regional system of P flows and stocks and was worded as follows: **What are the shortcomings and potentials in improving P management in the system of the region Berlin-Brandenburg, which arise from the interplay between different subsystems (e.g. agricultural sector and consumption sector) or factors taking influence from outside the system boundaries?** Secondly, a closer look at the agricultural sector i.e. agricultural soils, was taken. Here, the factors responsible for the high diversity in STP found in agricultural soils of the region were addressed. As this observation may be linked to farm management, the following question was put: **Can the wide range of P availability in soil as reflected by soil test P (STP) in the region Berlin-Brandenburg be related to specific characteristics of the farms or farming systems?**

1st research question

Based on the research presented in this thesis, a P SFA was compiled for the region to determine the flows, accumulations and deficits of P in the region. Previous work on this is partly outdated and does not look at the whole system (Behrendt et al., 1999; Kabbe et al., 2014; Lederer and Kral, 2015; MIL, 2012; Weyl, 1894). Other articles deal with larger or different administrative units and also do not consider the whole system and are also historical (Bach and Frede, 1998; Harenz et al., 1992).

As a result of this work, it was shown that in 2011 agricultural soils of the region were characterized by a negative P balance of -3,617 t P, which equals -2.74 kg P/ha within the boundary of State Brandenburg. As discussed, this result is supported by the fact that negative values have been frequently observed since the reunification of Germany in 1990 (Behrendt et al., 1999; MIL, 2012). For 2011 a crop offtake of 15,283 t P without straw and residues was determined. In 2006 only, an equally low P withdrawal was witnessed. It was further found that P offtake at harvest varies significantly (7,069 t P/yr between 2005 and 2013) depending on the successful cultivation of the main crops i.e. rape seed, cereals and maize. The underlying controlling factors for the investigated period are weather conditions, which in some cases interact with properties associated with the sandy soils of the region. This circumstance was used to speculate not only on future interactions between P in crop production but also on forestry and climate change, something that has, up to now, not been done by other authors. Such interactions may alter the success of growing certain crops and their potential to extract P from soils. Generally, higher temperatures in winter may result in better conditions for plant growth and P uptake. With winter rape seed, for example, black frost may be reduced, leading to less crop failures and higher P removal from fields. Also, increased temperatures could support P delivery to the root system and its subsequent uptake by plants, if soil moisture is sufficient and a possibly reduced snow cover does not interfere by letting the soil cool down further, slowing down soil P supply and P uptake. Due to alterations in annual precipitation patterns, P removal by organically grown winter cereals might be negatively affected as a result of an unfavorable release of N by mineralization processes, leading to reduced amounts of harvest. In general, this may also affect P released by decomposing organic matter. Water shortages due to less precipitation during summer, thereby resulting in lower soil moisture and a reduced groundwater table could affect plant growth and P uptake negatively as well and thus lower region-wide P removal by crops. Also, forest ecosystems may be affected in the same manner. For agriculture, such a change may result in the necessity to adjust recommendation schemes. Due to dry conditions, P emissions by wind erosion may be increased and heavy precipitation may aggravate this trend by increasing soil loss. A lower groundwater table, on the other hand, may reduce P losses to groundwater and through drainages while fewer freeze and thaw cycles could result in lower amounts of organic P being mobilized and emitted.

Considering the potential for agriculture in waste and wastewater, it was found that even in years of low harvest and thus low P offtake, the P in waste and wastewater flows of the region was not enough to forgo mineral fertilizer use in the agriculture of the region. However, with a total of 4,520 t P (3,588 t P retained from wastewater and 933 t P in waste) the amount of P in this source was still substantial, being of similar magnitude to the amount of P applied in mineral fertilizers in 2011 (4,477 t P). Most of the P in waste and wastewater was diverted to landfills. P in wastewater went to mono-incineration (30%), co-incineration (37%), landscaping (13%), agriculture (9%) and effluent (9%). P in waste was composed of bio-waste to incineration (73%), incinerated deceased livestock (11%), compost to urban soils (15%) and compost to agriculture (1%). Furthermore, diffusive losses from agriculture are of significant size (1,051 t P) possibly due to land excessively supplied with P or bad soil management. Another new finding was that biogas plants probably significantly increased P recycling in agriculture (2,490 t P). To which extent substrate imports were digested, however, could not be shown, leaving uncertainties about the amount of P being introduced from outside the region via this way.

Also, based on literature review (e.g. Newman, 1995; Tipping et al., 2014), the research highlights that there are still important unknowns connected to the P released by weathering and P deposited from the atmosphere, which have been generally neglected by other researchers in SFAs (e.g. Bateman et al., 2011; Cooper and Carliell-Marquet, 2013; Senthilkumar et al., 2012). These two aspects are shown to be especially relevant for low input systems such as forest soils of the region. Urban soils of the region were net accumulators of P (664 t P, equaling 1.97 kg/ha).

2nd research question

The second research question was addressed by conducting a letter survey in two counties (Barnim and Uckermark) of the Berlin-Brandenburg region, which was statistically analyzed by applying cross-tables and chi-squared tests. It could be shown that different ownership types responded differently to factors potentially taking influence on STP. Partnerships and companies/cooperatives were more susceptible to factors that cause lower STP than part-time and full-time individual farms. The latter, on the other hand, showed a tendency towards oversupplied land. Factors contributing to low STP were stockless organic farming, extensive cattle farming, grassland, and land tenure. Factors causing high STP were intensive livestock farming and biogas plants. To my knowledge, the P accumulating effect of biogas plants has never been described before, whereas the observation that intensive livestock farming coincides with higher STP in soils is a common finding (e.g. Csathó and Radimszky, 2009; Rubæk et al., 2013). Also, deficits in P management in organic farms with no livestock have been reported before by other authors (Foissy et al., 2013; Kirchmann et al., 2008). However, low to moderate STP in organic farming may not necessarily be connected to stockless organic farming (Nesme et al., 2012). The negative effect of extensive cattle farming and grassland as such could not clearly be elucidated. It was supposed that focusing on other aspects in agricultural production or financial difficulties in the system of production led to shortcomings in soil management. However, more information on this observation would be needed in order to draw conclusions. The negative effect of land tenure has been described before (Myyrä et al., 2005) and may have even been aggravated by the specific land allocation policies in East Germany (Jochimsen, 2010). It should also be noted that leased land may already have been in a worse condition as land with a lower production potential may be more likely selected for lease (Akerlof, 1970). As shown, some observations of this work have already been described in the literature, but not yet for the regions under study or Germany as a whole and are therefore new.

6.1 Critics on Methods and Prospects for Improvement

1st research question

As stated by Jedelhauser and Binder (2015), setting up an SFA is a labor intensive and time consuming task. To obtain a comprehensive picture of the P flows of the region Berlin-Brandenburg, extensive research and screening of various different documents from regional and national statistics and scientific literature was needed and numerous people in different positions working for administration or private companies had to be interviewed. Thus, the compilation of an SFA would be greatly facilitated and accelerated, if databases containing information on material flows and P contents were provided by administration or the scientific community. With the aid of such a tool, time series could be easily established, which would enable a straightforward identification of trends in P flow dynamics. Information gathered in this way could foster positive development and avoid the negative. In addition, the preparation of P data bases would also be useful in providing first quantitative insights into the most relevant processes without having to elaborate an entire web of P flows of the whole system. At the same time, the performance of further analyses, such as a cluster analysis, could be facilitated (Jedelhauser and Binder, 2015). Jedelhauser and Binder (2015) suggest that data by FAOSTAT, EUROSTAT or the World Bank should be further expanded by P-related data. In addition, the authors recommend a standardization of SFAs to ensure a comparability of different systems. Doing so, they provided a blueprint for future SFAs (Jedelhauser and Binder, 2015).

Generally, constraints in data collection arise from the potential violation of business secrets, limited entitlement by the law, and the lack of influence on how and if data are collected. It is also important to mention that the information necessary to compile an SFA does not only comprise the quantity (material) and quality (e.g. P content and contamination) of a flow but also the direction to where it is going (exported or forwarded to another process within the system). This is because wrong assumptions on pathways can significantly distort the outcome of an analysis. In any case, a further involvement of governmental bodies needs to be even more highlighted since the SFA method serves as a kind of feedback loop to policy changes. This view is supported by Jedelhauser and Binder (2015).

However, it has to be considered that SFAs alone may not appropriately reflect problems associated with P management. As already shown in this thesis, mismanagement of resources may appear in spheres not accessible to SFAs, which in these cases observed here, was related to the high number of players involved (e.g. waste management companies or farmers in agriculture). However, once these factors are known, appropriate means may be implemented to obtain a higher resolution of flows. Further, SFAs need to be complemented by various other methods such as a stakeholder analyses to unfold their full value. As outlined by Jedelhauser and Binder (2015), multi-level legislations such as directives, laws and ordinances regulate resource management and political agendas and paradigms can quickly change the shape quantity of flows. Additionally, the high number of actors and actor groups have different time horizons and goals. This might result in conflicts of interest.

Although increasing efforts are spent on this topic, up to now there is no uniform, standardized way of handling uncertainties in SFAs (Jedelhauser and Binder, 2015; Laner et al., 2014). A big problem in handling uncertainties is that, in many cases, limited data availability impedes a proper estimation of the actual variation of a flow, leading to the classification of estimated uncertainties in uncertainty ranges which, at least to some extent, is based on educated guesses (Antikainen et al., 2005; Laner et al., 2014). To avoid this problem Laner et al. (2015, 2014) suggest that using the 'fuzzy set' theory may be a promising method.

2nd research question

The fact that similar linkages between farm structural factors and STP are found in other studies supports the validity of this work and backs the credibility of the findings that have not yet been reported (effect of ownership type and biogas plants). This debilitates criticism of the methods employed (letter survey), which are connected to the problem that farmers themselves indicated all the information and may therefore try to veil unfavorable soil conditions, having disregarded recommended best practices regarding soil management. However, although the number of participants is relatively high, it is also evident that there is still a considerable share of farmers who did not participate in this survey although they had the possibility to do so. Reasons for this may be multiple, ranging from mistrust or indifference to simply not having sufficient time to answer the questions. In addition, although not mentioned in the research article, the conformity of county data provided by the LELF with that of the survey (figure two in the article: "P availability and farm structural factors: examining scarcity and oversupply in north-east Germany") should still be noted with caution. A coincidence cannot be excluded here.

6.2 General Implications

1st research question

With respect to the first research question, to determine regional inputs, it would be of great value, if there were more data on the consumption and trade of imported feed and fodder, in order to derive the proportion of imported P in animals, animal products and animal excreta. Similarly, statistics on substrate use in biogas plants, which give information on their source (from inside or outside the regional system), would enhance the accuracy of the model. If this data was available, potential additional inputs of the derived substrates to the soils of the region could be determined. This may, in turn, affected the calculated P balance of these soils. Furthermore, deceased livestock that, due to hygiene issues, would have to be disposed of without any further use, could be considered for P recycling. Burning their remains in a mono-incineration plant along with sewage sludge, with a subsequent extraction step to recycle the P contained therein, should fulfill sanitary standards and at the same time reintroduce P for further use. Generally, increasing the share of mono-incinerated sludge is desirable to ensure a future recycling of P by avoiding its dilution, if no other recycling measure is feasible. It also seems advisable to rethink the management of organic wastes to increase the recycling of contained P. Local composting or digestion of these wastes may be regarded as an option to overcome problems associated with the transport of waste in areas of low population density. Also, organic substances, being rich in P (such as sewage sludge), may be better exploited for the P use in agriculture instead of being employed for landscaping and construction purposes. Substrates with lower P contents like compost from urban regions could be used instead. This would to a small extent at least reduce the high P stocks in urban soils. In addition, an effort could be made to create awareness to further lower the consumption of animal based food. The same applies to reducing waste along the food supply chain.

2nd research question

It is important to notice that the interactions of nutrient flows with agricultural policies and farm structures are rather complex. Thus, the results of the second study should not be used to condemn certain ownership types or business forms as scapegoats. Such a practice would likely, for good reason, lead to a reduced farmer participation in future surveys, making difficult the identification of and interference with external negative developments. In contrast, the results of this study should help to provide measures for agricultural businesses for dealing with an unbalanced STP in their agricultural land. Considering the discussed literature, it is likely that the observations made are also applicable to other regions in Germany, Europe or the world and should therefore be taken into account in the design of new policies, not only in the study region. It may also be proposed that more controlling and regulating feedback loops between practitioners and policy makers are desirable.

6.3 Future Research

Based on this thesis, future research may look at improving possibilities for recycling P from waste and especially wastewater streams. Regarding the recycling of P from wastewater further research on the charring of sewage sludge (sewchar) may be suggested (Breulmann et al., 2015; Caballero et al., 1997; Van Wesenbeeck et al., 2014). If this treatment is employed, sewage sludge could be sanitized and organic toxins eliminated. Given that energy costs are not too high, such a simple measure could be an option for sewage sludge low in heavy metals, especially when the application of sewage sludge is no longer allowed. Also, certain organic wastes needing sanitation may be treated this way. Such a practice would not only recycle P and other nutrients, but could potentially make use of the positive effects of biochar on soil.

Another interesting aspect could be the investigation of soil P legacy from former P application in the region and how it could be efficiently employed to contribute to agricultural production (Rowe et al., 2015). Here, methods increasing the mobilization of soil P stocks may be of interest. When considering soil P, the question of the right level of P in soils arises and whether current recommendation schemes for P application could be changed in order to improve P management (Römer, 2013). As discussed in this thesis, recommendation schemes may not only need to account for soil parameters, but may also need to look at the climatic characteristics of a region. In connection, the impact of climate change may need to be accounted for in future. Further, new and maybe more accurate technologies, such as the DGT technique could be included in recommendation systems (Six et al., 2013, 2012). With respect to the high share of land being classified as undersupplied in P and the reports on diminishing P fertilizer use and P deficiency in agricultural soils (Behrendt et al., 1999; Heidecke and

Roschke, 2008; MIL, 2012; Zimmer and Ellmer, 2012), it would be interesting to ask in how far plant growth and yield are affected by P deficiency.

In view of the P emission from agriculture (IGB, 2014), it may be asked how P losses from agriculture can be reduced. Here, management strategies are likely to provide promising answers. In this context, more knowledge on wind erosion would be valuable. Research should also envisage shedding light on P released by weathering and (net) atmospheric deposition flows, as these flows are of great importance for the balance of low input forest soils. Additionally, agriculture may benefit from a broader knowledge of these flows. As shown in this thesis, the amount of P that passes through biogas plants has reached significant importance. As currently sources on this flow only allow for an approximate quantification, future work could try to obtain a more sophisticated estimate, if new sources for calculation are provided. Questions connected to this are: How much do biogas plants contribute to inner regional P recycling and its inner regional accumulation? And how much is the contribution of imported substrates? One may also ask about the impact of biogas plants on other (nutritional) elements. However, asking for reasons for the inner P accumulations or the regionally unequal distribution of STP is especially interesting since recommendations provided by authorities are poorly followed as demonstrated by the EU27 (Csathó and Radimszky, 2009). The overall picture given by the information gathered and gained in this thesis shows there were multiple reasons responsible for this. Especially, considering short term developments, the inner regional distribution of P in agricultural soils may be more problematic than the region wide balance. For Brandenburg in particular, rising prices for land, a diversity of lease contracts and the fact that privatization of agricultural land, which previously had been passed into public ownership in the GDR, is still ongoing and (Jochimsen, 2010) may provide relevant research questions. Also, similar to pH and lime application, STP could be used as an indicator for land related investments and soil conservation. Its explanatory power, however, may be limited, since certain management practices may lead to land being oversupplied with P, when agricultural land is merely considered as a dumping site for excess nutrients. On the other hand, farm management aspects fostering excess application of P may be identified more easily than those leading to poor STP, since accumulation can appear at faster rates than the withdrawal of P by plant uptake. Other aspects that were not tackled by the survey were the effect of the distance of a field from the farmyard or the source of nutrients in general. For example, Myyrä et al. (2005) found that farmland further away from the farmyard may exhibit lower STP and pH values. Also, further research could have a closer look at different livestock production strategies, such as dairy versus meat farming and their connection to P management, as no answer to this question could be given in this work. Other management characteristics may be plowing depth or crops in production. Generally, it will be very useful to distinguish between arable land and grassland with respect to STP and the assignment of P flows. It may well be that grasslands are depleted of their P in favor of arable land.

As a result, it is clear that further research on farm structures and their effect on STP, and also farm P management in general should be encouraged. Without doubt farm structural factors represent a highly relevant source of information for different degrees of efficiency in P management.

Looking beyond the scope of this thesis and also beyond the region, new, out of the box approaches could be envisaged. One interesting approach for management may be the production of (water) plants on open waters (Radulovich, 2011). As eutrophication has led to a widespread manifestation of dead zones in the oceans along coast lines (Altieri and Gedan, 2015) it may be advisable to use these areas for the production of food, fodder or fuel. As well as obtaining a marketable product, this practice would allow for nutrients to be captured and reintroduced to the anthroposphere, while at the same time environmental problems could be alleviated and pressure on land and water resources could be reduced (Radulovich, 2011). Another possible improvement might lie in insect rearing. Due to the adoption of insects to many different ecological niches, insects are endowed with the ability to feed on many different substrates and potentially also a variety of organic side-streams. Here, regarding P, symbiotic relations between insects and bacteria could be employed for increasing P use efficiency. In the gut of a larvae of the beetle species *Batocera horsfieldi* (Cerambycidae), for example, phytate digesting bacteria were found, which help the beetle to breakdown the phytate contained in their feed (Zhang et al., 2011). As phytate, cannot be digested by non-ruminant livestock and humans, it reduces the bioavailability of essential elements like Ca, Fe and Zn and prevents the P bound therein from being accessed (e.g. Cowieson et al., 2006; Kumar et al., 2010). This example shows that insects could also play a valuable role in tapping phytate containing flows by simultaneously reducing the adverse effects of phytate not only in the nutrition of livestock, but also that of humans. Particularly, in developing countries where the consumption of insects is common (FAO, 2013) and malnutrition is a frequent problem for which the addition of phytases[4] to food has already been proposed as a solution (Kumar et al., 2010) this could be an interesting approach. Moreover, a recent study prospected that assuming a continuously increasing growth of income, by 2050, global

[4] Enzymes that catalyzes the hydrolysis of phytate.

animal-based food demand and therefore P intensive food production will grow considerable, outpacing the average increase in total food consumption with growth rates of presumably 175 to 233%. This increase will be strongest for tropical and subtropical regions such as Sub-Saharan Africa and South Asia (up to 9 fold) (Bodirsky et al., 2015).

Regarding the increasingly available information technologies, such as smart phone apps, Shepherd et al. (2015) proposed their employment in improving famers P management (e.g. crop and fertilizer management, trade of agricultural P sources) and the provision of relevant data to authorities or the scientific community. In analogy to this, such tools could contribute to P use efficiency, also in other areas, to trace P flows. Thinking of society as an anthropogenic metabolism parallel to the urban metabolism (Lederer and Kral, 2015; Weyl, 1894) these apps would represent receptors, like in organisms, enabling feedback loops that could help to monitor and manage many different life sustaining commodities. However, such an approach also has to be seen critically, since crowd founded data may not be reliable or the privacy of actors may be violated. Generally, it should be taken into account that P in flows is often accompanied by other valuable elements or nutrients that may be mined as well, creating beneficial synergistic effects for the management of P and other substances.

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